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PEABODY MUSEUM ARIZONA EXPLORATION, 1920

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The season's field work allows us to delineate more clearly than has hitherto been possible the archaeological problems of the Kayenta district in northeastern Arizona. It seems best to give: first, a summary of our previous knowledge; second, an account of the new material brought to light; third, an outline of the present status of the investigation.

1. *Previous Knowledge of the Archaeology of the Region.*—The earliest culture was that of the Basket-makers, a dolicocephalic people who did not practice skull deformation, did not build permanent dwellings, had no pottery, did not grow cotton or beans or domesticate the turkey. They cultivated corn of a single simple variety. Typical arts were: the weaving of excellent coiled baskets, square-toed sandals, twined bags, fur-string robes. They used the spear-thrower and dart instead of the bow and arrow.

At a somewhat later period the country was inhabited by the Slab-house people (so named by the present authors). While their culture, known only from two or three badly preserved sites, was little understood, the following traits were recognized: the settlements were loose aggregations of small, round or oval, semi-subterranean rooms, with foundations of upright slabs and stone and adobe superstructures. The pottery was of two sorts: a well decorated black-on-white painted ware, with characteristic designs; and a rudimentary coiled ware with a few heavy, broad corrugations about the necks of the jars. Nothing else was known, not even such important features as skull-type, burial customs, textiles, basketry, sandals and agricultural products. Stratigraphic finds, however, had made the chronological position of the culture clear; it was earlier than the Cliff-dweller-Pueblo and later than the Basket-maker.

The third and latest group of remains was the Cliff-dweller-Pueblo. It was well known from the investigations of Cummings, Fewkes and the

authors. Its leading traits were: houses of coursed masonry, the rooms rectangular and arranged in series to form, when the site permitted, definite pueblos; subterranean ceremonial rooms or kivas; crania with strong occipital deformation and apparently originally brachycephalic; cultivation of several varieties of corn, as well as of cotton and beans; domestication of the turkey and use of its plumage for feather-string cloth; use of the bow and arrow; manufacture of great quantities of pottery of distinctive types, black-on-white, red-and-yellow, red, and corrugated.

The interrelation of the above three groups was not understood. The Basket-maker was obviously the earliest, the Slab-house next, and the Cliff-dweller-Pueblo latest; but whether they were to be regarded as stages in the development of a single people, or whether they represented successive occupations of the region by two or even three different tribes, could not be decided on the basis of the evidence available.

2. The explorations of 1920 in Sagi Canyon have added many new data. A few Basket-maker remains were found in various caves; these ran entirely true to the previously established type and, as usual, showed no admixture of later material (Slab-house or Cliff-dweller-Pueblo). Furthermore, a hitherto unrecognized culture came to light. At the west end of a large cave were unearthed rooms with slab foundations and stone and adobe superstructures; in and about the rooms was rubbish which yielded the following material: rough undecorated pottery of distinctive shapes, mostly black, some gray, a very little red, no trace of coiling; many sandals elaborately decorated in relief work and in colors, with a broad scallop across the toe end of each; handsomely ornamented woven carrying straps; crudely made twined bags. There was no cotton or turkey-feather cloth. In front of the cave lay a small burial mound containing skeletons with long, undeformed crania and accompanied by pottery identical with that from the rooms.

In the same cave, but farther to the east were discovered burials of the Slab-house culture; the identification was made by means of typical Slab-house vessels deposited with the bodies. The individuals had strongly deformed skulls. With them were: a large decorated carrying basket of a type not found with Basket-maker burials; cotton cloth; turkey-feather cloth; a complete bow and part of another; a twilled yucca ring-basket; a carrying strap of Cliff-dweller-Pueblo type; and a piece of rush matting. No house-structures associable with these graves were found, but the site was only partially excavated.

At the eastern end of the cave was a group of typically Cliff-dweller-Pueblo rooms, containing an equally typical assortment of pottery, textiles, sandals and other objects of the Cliff-dweller-Pueblo period.

3. *Present Status of the Investigation.*—The Basket-maker culture is still to be considered the earliest in the region. A second culture, which we call the Post-Basket-maker, followed the Basket-maker. Its probable

descent from the Basket-maker is indicated by the dolicocephalic bead form and absence of cranial deformation; by the elaborateness of the sandal weaves; the presence of a degenerate type of twined-woven bag; and by the use of fur cloth instead of feather cloth. The absence of cotton from both cultures should be noted. Advances over the Basket-maker are seen in the appearance of pottery (albeit of a crude type), in the presence of permanent house-structures, and in the elaboration of the carrying straps.

The third culture is the one which we formerly called the Slab-house. As that term, based on a feature of the architecture, is equally applicable to the Post-Basket-maker we have discarded it and substitute the name Pre-Pueblo. This group is allied to the preceding one most closely apparently in house-types, and in the possession of pottery, though its characteristic wares are much the more highly developed of the two; it differs sharply from the Post-Basket-maker in the practice of skull deformation, in the possession of cotton, turkey-feather cloth and twilled basketry. Traits that it shares with the succeeding culture, the Cliff-dweller-Pueblo, are: skull deformation; decorated pottery; cotton; turkey-feather cloth; the bow.

From the above data it seems probable that the Basket-makers were the direct ancestors, both physically and culturally, of the Post-Basket-makers; the latter, however, had made considerable advances (houses, pottery). A direct line of descent from Post-Basket-maker to the Pre-Pueblo might be inferred from the similarity in house-types; but the Pre-Pueblo are in most respects much more nearly allied to their successors, the Cliff-dweller-Pueblo people, than they are to the earlier group.

To sum up: Basket-maker is probably ancestral to Post-Basket-maker; Pre-Pueblo to Cliff-dweller-Pueblo; the genetic relationship of Post-Basket-maker to Pre-Pueblo may be inferred, but is still doubtful. A more detailed knowledge of the material cultures of the two middle groups is necessary, as well as studies to determine whether or not skull deformation alone is capable of producing the marked appearance of brachycephaly exhibited by the crania of the two later groups.

THE OPEN MERCURY MANOMETER READ BY DISPLACEMENT INTERFEROMETRY[1]

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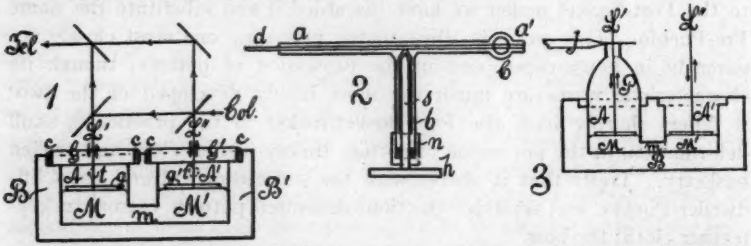
1. *Apparatus.*—This is practically a U-tube, AmA', figure 1, with wide shanks, AA', connected by a channel, m, below. A and A' are cylindrical hollows, 2–3 cm. deep and about 5 cm. in diameter, cut in a rectangular

[1] Advance note from a report to the Carnegie Inst. of Washington, D. C.

block, BB', preferably of iron. The connection m must also be large in section, so as to admit of rapid flow from A to A'. The U-tube is charged with mercury MmM', M and M' being as shallow as possible to counteract the tendency to vibration. Thin plane parallel glass plates, gg', round discs of equal thickness and diameter, are floated on the mercury, which act as mirrors for the interferometer beams, L' and L'', and also materially check the tendency of the pool of mercury to vibrate. It would be desirable to be able to use the mercury surfaces at M and M' directly without the intervention of the plate; but within the city limits the fringes are unsteady and hard to find.



The top of the iron block BB' is recessed as shown, to receive the plane parallel glass plates GG'. These like gg' must be equally thick; otherwise the fringes will be multiplied and faint. The annular space $cccc$ between G and B is filled with resinous cement, poured in in the molten state. The air space AA' shut off in this way communicates with the atmosphere by two tubulures, t and t', in the front side.

The ray parallelogram of the quadratic interferometer of which $L'L''$ are the interfering rays should be vertical. The displacements of the achromatic fringes of white light are read off by a telescope with an ocular micrometer (scale part 0.01 cm.). The fringes parallel to the divisions of the micrometer are conveniently made a scale part in size. The block BB' should be mounted separately from the interferometer. If it is placed on the base of the latter, all manipulations there shake the mercury in BB' and it is necessary to wait for subsidence. This, however, occurs very soon, so that the separate mounting is not absolutely necessary. Without manual interference the fringes are about as quiet as in a solid apparatus.

2. *Experiments.*—To test this apparatus the air space AA' was left with a plenum of air. With A' communicating with the atmosphere, A was joined through t and a filimentary capillary glass or metal tube, to an apparatus by which slight pressure could be applied. In the first trials I attempted to use a water manometer controlled by a micrometer screw; but the vibrations of the meniscus were at once impressed on MM' so that the fringes were hard to keep at rest. I then devised the apparatus shown in figure 2, which is merely an adaptation of the pin valve of an oxygen tank, with a good micrometer screw, s, and stuffing box, n. The

head h of the screw is graduated. The barrel b is at right angles to the tube aa', which at a joins the capillary tube d, leading to t of figure 1. At the end a' there is a cock, C, which shuts off communication with the atmosphere. Thus when C is closed pressure is applied directly at A, figure 1, by rotating the head h in figure 2. This pressure is at once removed by opening C.

The apparatus worked surprisingly well. When C is closed and h rotated, the fringes may be placed anywhere in the field about as conveniently as with the micrometer screw at the mirror of the interferometer. There is, however, one difficulty which I have not thus far been able to remove. When the pressure increments exceed a certain small value, the plates gg' no longer rise and fall in parallel. The coincidence of images is destroyed and the fringes vanish. There is here a conflict with the capillary forces present at the edges of the disc. I endeavored to improve this by using small plates gg', anchored near the centre of MM' by 4 loose threads. But the advantage was not marked. Fringes a scale part in size will not be available for more than 50 scale parts, being sharpest in the middle. This is about half the diameter of field of the ordinary telescope. Curiously enough, fringes from the free surfaces of mercury vanish in the same way, probably owing to surface viscosity of the mercury, not absolutely pure.

3. *Equations and Pressure Observations.*—If the cock C, figure 2, is closed and the temperature for brief intervals is considered constant, Boyle's law may be written (ignoring signs of increments)

$$\frac{dv}{V} - \frac{dV}{V} = \frac{dp}{p} = \frac{dh}{76} \qquad (1)$$

where V is the total volume enclosed, dv the increment at the micrometer screw hs, and dV the corresponding decrement equivalent to the pressure decrement dp. If a is the area of the piston at g $dV = a\,dh/2$ and if $V = aH$, H being the corrected air space at A, equation (1) becomes

$$\frac{dv}{V} - \frac{dh}{2H} = \frac{dh}{76}. \qquad (2)$$

But dh on the interferometer is equivalent to n fringes of wave-length λ so that $dh = n\lambda/2$. Hence, finally

$$dv = V\frac{\lambda}{2}\left(\frac{1}{76} + \frac{1}{2H}\right)n. \qquad (3)$$

This equation gives a test of the trustworthiness of the gauge.

In the apparatus used the following constants were found by measurement: $V = 66.8$ cm.^{3}, $a = 29.2$ cm.^{2}, $H = 2.29$ cm. The pitch of the screw was 0.073 cm. and its mean diameter 0.51 cm. Hence per turn $dv = 0.073 \times 0.204 = 0.0149$ cm.^{3} and $dv/V = 10^{-4} \times 2.23$ per turn. The mean wave-length being $\lambda = 6 \times 10^{-5}$ cm. equation 3 reduces to $n = 3.2$ fringes per turn of the screw hs.

In the experiments fringes of 1/2 scale part were installed. In separate experiments immediately after closing the cock C, a half turn of the screw produced a displacement of 8.3, 8.0, 8.0, 8.5, 8.5 scale parts, as the average, therefore 16.4 scale parts per turn or about 33 fringes per turn. This agrees as closely as may be expected with the number computed.

The pressure increment per turn of screw is $dp = n/2$ cm. of mercury or per turn of screw about 10^{-3} cm. Per fringe, therefore, 3×10^{-5} cm. of mercury as anticipated. A range of about 2 or 3 turns of screw was possible with each fringe, i. e., the range of pressure measurement should be from 3×10^{-5} to 3×10^{-3} cm. of mercury.

Experiments of the same kind were made in great variety. There is no difficulty in using much larger fringes so that 3×10^{-6} cm. of mercury should be appreciable. By exhausting both sides of the U-tube the apparatus becomes a vacuum gauge. I did not, however, attempt much work with it as the present apparatus was not well adapted for the purpose.

Air Thermometer.—If the cock C is permanently closed, the air space A becomes the bulb of an air thermometer of approximately constant volume. In this way the heat produced by the rays of light L' may be measured. In a variety of experiments of the kind, the mean result was about 10 scale parts or 20 fringes in a lapse of 210 seconds. If τ denotes absolute temperature, the intrinsic equation may now be written

$$\frac{dp}{p} + \frac{dv}{V} = \frac{d\tau}{\tau},$$

which reduces as above to

$$\frac{dh}{76} + \frac{dh}{2H} = \frac{d\tau}{\tau}.$$

Thus if $\tau = 300°$

$$d\tau = \tau n \frac{\lambda}{2}\left(\frac{1}{76} + \frac{1}{2H}\right) = 10^{-3} \times 2.1n° \text{ C.}$$

and for $n = 20$ in 210 seconds

$$d\tau = 0.042° \text{ C.}$$

or the heating produced was $2 \times 10^{-4}°$ C. per second. Whether, supposing AA' to be filled with water, a pyrheliometer may be constructed on this principle I have yet to learn.

Other interesting results of the same kind might be mentioned. Thus if the screw stopcock, figure 2, is closed quickly (C being open) there is always a decided increment of pressure. In other words in consequence of the viscosity of air, the fine space at the plug is virtually a closure before the screw is checked by an actual closure.

If the glass plates G are removed and the air space A is closed by a pipe, P, tapering to a neck as in figure 3, it becomes a closed organ pipe adapted for the measurement of acoustic pressure. It may be blown by an adjustable embouchure, j, described heretofore (*Science*, **53**, 1921 (47)), or

by resonance. Thus far, however, I have failed to find more than a pipe sounding under slightly increased or slightly diminished pressure.

Again if the apparatus, figure 3, is made of insulating material (*P*, *j* removed) and is provided with a disc electrode parallel and coaxial with the surface *M* used as a counter-electrode, the combination becomes an absolute electrometer of considerable interest. All the usual experiments of the electroscope may be performed by means of it, with the potential readings immediately in absolute units.

STUDIES ON CATALYSIS. I—THE REDUCTION OF URACIL TO HYDROURACIL

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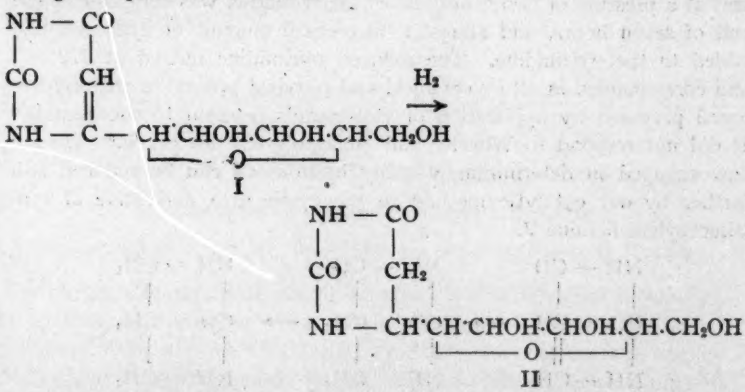
Communicated February 1, 1921

Levene and LaForge,[1] in 1912, made the interesting observation that the nucleoside *uridine* I, which is obtained by hydrolysis of nucleic acid, is reduced practically quantitatively to dihydrouridine II by Paal's[2] method of catalytic reduction, namely, by means of colloidal palladium and hydrogen. This transformation involves an addition of hydrogen at the double bond joining positions 4 and 5 in the uracil nucleus and the change is represented as follows:



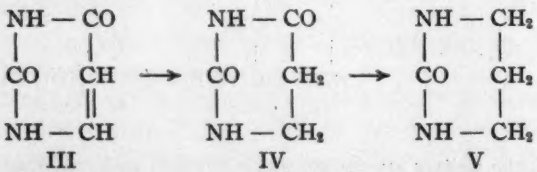
As far as the writers are aware, this is the first and only case described in the literature of the application of a catalytic process of reduction in the pyrimidine series. A striking fact revealed by the work of these investigators is the remarkable ease with which the sugar can be detached from this dihydrouridine molecule II by hydrolysis with acids. The corresponding uridine combination I is very stable and resistant to hydrolysis.

We have now inaugurated in the Sheffield Chemical Laboratory an extended research dealing with the application of catalytic methods of reduction and oxidation to pyrimidine, purine, hydantoin and glyoxaline compounds, and in this paper, the first of our series, we record the results obtained by direct reduction of the pyrimidine *uracil* with colloidal platinum.

The process which we have applied successfully for the reduction of uracil is based on the method of reduction developed by Skita.[3] This investigator used both colloidal palladium and platinum in his work and utilized as a support for his colloidal metal gum arabic. He showed also that his colloidal metals were active in both acid and alkaline solutions.

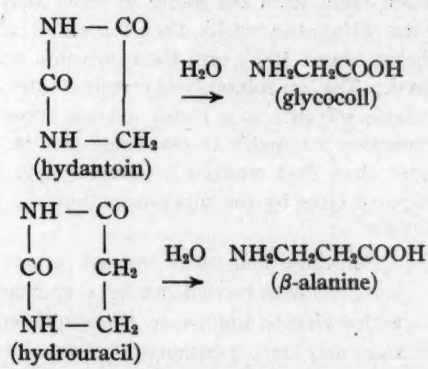
In our process we make use of a 10% solution of hydrochloroplatinic acid for preparation of our colloidal metal, and precipitate the activated metal in an aqueous solution of gum arabic by reduction with hydrogen gas without first introducing any colloidal metal to promote the reduction of the platinum chloride solution. Skita used in many cases a promoter to stimulate the formation of colloidal metal (Impfmethode). This was prepared by reducing platinum solution with formaldehyde in alkaline solution.

At a pressure of two atmospheres uracil III is reduced nearly quantitatively in aqueous solution to hydrouracil IV by action of hydrogen gas in presence of colloidal platinum. For example, when six grams of this pyrimidine were agitated in the reductor at a temperature of 75–85° C. and at a pressure of two atmospheres the reduction was complete at the end of seven hours, and almost a theoretical amount of hydrogen had added to the pyrimidine. The reduced pyrimidine melted at 272° C. and corresponded in all its chemical and physical properties with hydrouracil prepared by application of Hoffmann's reaction to succinimide.[4] It did not respond to Wheeler and Johnson's test for uracil.[5] We are now engaged in determining whether hydrouracil can be reduced still further by our catalytic method to the cyclic urea derivative of *syn*-trimethylenediamine V.



From both a biochemical and a synthetical point of view the synthesis of hydrogenated uracils by direct reduction of the pyrimidine ring is a reaction of considerable importance. These reduced uracils bear a similar relationship to β-aminoacids as the hydantoins do to α-aminoacids. A practical method of reducing uracil combinations, therefore, opens up a new method of synthesizing representatives of this important class of

aminoacids. The above relationships are expressed by the following equations:



Before undertaking our research on catalytic reductions we devised a practical machine whereby we might operate on a quantitative basis with large quantities of reagents. A description of this machine and a complete record of our preliminary work on uracil reduction will be published in a future number of the *Journal of the American Chemical Society*.

[1] *Ber.*, **45**, 1912 (619).
[2] *Ibid.*, **37**, 1904 (124); **38**, 1905 (1398, 1406).
[3] *Ibid.*, **45**, 1912 (3579, 3595).
[4] Lengfeld and Stieglitz, *Amer. Chem. J.*, **15**, 1893 (221).
[5] *J. Biol. Chem.*, **3**, 1907 (183).

THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY

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For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing-points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so alike to it chemically that compound formation between them shall be at a minimum. To be restricted in the choice of solvents is, therefore, a disadvantage. Boiling temperatures are preferable to freezing temperatures as disfavoring the formation of exothermic compounds. A majority of organic compounds boil nor-

mally below 300° C. If, as is true, the solvent must differ by at least 150 degrees in boiling-point from the solute in order that the volatility of the latter shall not vitiate the results, then the use is indicated of such solvents as boil below about 100°, and these solvents are indeed those most commonly used. The low solubility of certain solutes at the freezing-points of the available solvents is a factor against cryoscopy. On the other hand, the precision attainable in cryoscopy has, in the past, been considerably greater than that realized in ebullioscopy, even with apparatus fortified against error by the superimposition of a multiplicity of paraphernalia.

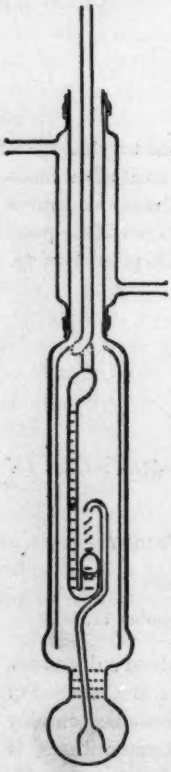

FIG. 1

For these and other reasons, a very great deal of work has been carried out by very many investigators with a view to improving the ebullioscopic technique. One may but mention the two dozen papers by Beckmann and his collaborators;[1] and the work of Hite,[2] Orndorff and Cameron,[3] Jones,[4] Ross Innes,[5] Meyer and Desamari,[6] Drucker,[7] Sakurai,[8] Landsberger,[9] Walker and Lumsden,[10] McCoy,[12] Smits,[13] Rijber,[14] Ludlam,[15] Erdmann and Unruh,[16] Lehner,[17] Turner.[18] Even a single publication by one writer—Hite—reports the trial of over 100 different forms of apparatus. In all these, and many other investigations, the bulb of a mercurial thermometer has been submerged beneath the surface of the boiling solution, and much of the work has been directed to the avoidance of the consequent irregular superheating. In our opinion, the two most successful improvements made since 1892 have originated in this country, the introduction, namely, by Bigelow[19] of electric heating, and by Cottrell[20] of a "lift-pump" which pumps the solution over the bulb of the thermometer, which no longer need be submerged in the solution, but is located above the solution in the vapor phase. When Cottrell's device is employed, there remain outstanding the errors inherent in the Beckmann type of thermometer, the error due to uncertainty as to actual concentration, and the very serious error due to change of boiling-point caused by change of barometric pressure during the observations. This last may, in part at least, be overcome by the employment of somewhat cumbrous "manostats,"[21] by especially constructed aneroid barometers,[6] or by the use of a second, duplicate, apparatus[22] operated simultaneously and containing another Beckmann thermometer immersed in the pure boiling solvent.

In 1910, Menzies[23] had described a simple apparatus, independent of

barometric change, which gives molecular weights of solutes at their boiling-points by direct measurement of lowering of vapor pressure, without the use of any thermometer. Continuing this effort at simplification, he found that the application of the differential thermometer of the preceding article to ebullioscopy with the Beckmann type of apparatus served only to render more glaring the inevitable irregularities inseparable from that method of procedure. When, however, Cottrell's paper appeared in 1919, the first opportunity was taken to secure collaboration in working out the simplest possible apparatus and technique which should free ebullioscopy from all its most serious drawbacks.

The diagram, fig. 1, shows a boiling tube, whose narrowed upper portion itself serves as condenser tube. A glass cylinder, open above and below and of diameter slightly less than the boiling tube itself, is located concentrically within the latter, and confers the advantages of a double jacket. Within this is supported the differential thermometer, on the lower bulb of which hangs the pump, loosely, as a hat on a peg.[24] The absence of rigid connection diminishes breakage, besides adding flexibility, literal and metaphorical. The boiling tube is heated by a common Bunsen burner, with a low flame protected by the customary metal draught-shield. When boiling begins, portions of the liquid in the bulb are carried by the vapor in fragments up the pump and discharged to form a thin film over the lower bulb of the thermometer, which thus attains the temperature at which this liquid, or solution, is in equilibrium with the vapor. The upper bulb acquires the temperature of the pure boiling solvent. The thermometer registers the difference between these two temperatures. Equilibrium is reached so rapidly that fresh additions of solute may be made as fast as they can be weighed out. Contrary to all ebullioscopic tradition, the apparatus will give good results in a room that is not free from draughts. Unlike every other ebullioscopic apparatus, this form is entirely free from all corks, ground glass joints or stoppers.

The sources of error, especially that due to barometric change, eliminated by the use of the new type of differential thermometer have been briefly referred to in the preceding article. The advantages gained by removing the lower bulb from immersion in the boiling liquid have been well explained by Cottrell[20] and confirmed by Washburn and Read.[25] The chief residual source of error lies in the uncertainty as to the true concentration of the boiling solution as deduced, not by subsequent analysis, but simply from the weights of solvent and solute used. Part of the solvent is absent from the solution in the form of condensate on the walls, and part is absent in the form of vapor. This source of error, ever present in the Beckmann type of apparatus, has often failed of due consideration. To minimize it, we constrict the boiling tube above the lower bulb, mark cc. graduations on the cylindrical neck so developed, and read off the actual working volume of the solvent an instant after causing ebullition to cease, while

the tube is still wet with condensate and filled with vapor.

A simple water-filled differential thermometer suffices for the range of temperature from the boiling-point of water to that of ether, thus embracing the use of such other solvents as carbon bisulphide; acetone; chloroform; methyl, ethyl and propyl alcohols; ethyl formate, acetate and iodide; carbon tetrachloride and benzene; and allowing a choice adequate for ordinary purposes. No "setting" of the thermometer for the use of different liquids is required.

Details of procedure and of results will be given in more complete publications elsewhere. Different sets of determinations with the same materials, carried out on different days, yield results concordant within one-half of one per cent. In spite of the simplicity of the apparatus, we venture to think that this form of the ebullioscopic method compares favorably with the customary form of the cryoscopic method in ease and speed of operation as well as in precision of results.

[1] References to the numerous papers of Beckmann and his collaborators may be found in the work of Jellinek, C., *Stuttgart, Lehrbuch der Physikalischen Chemie*, **2**, 1915 (783 et seq.).

[2] Hite, *Baltimore, Md., Amer. Chem. J.*, **17**, 1895 (514).

[3] Orndorff and Cameron, *Ibid.*, **17**, 1895 (517).

[4] Jones, H. C., *Easton, Pa., The Freezing-Point, Boiling-Point and Conductivity Methods*, 1912.

[5] Innes, R., *London, J. Chem. Soc.*, **81**, 1902 (682).

[6] Meyer and Desamari, *Berlin, Ber. deut. Chem. Ges.*, **42**, 1909 (797).

[7] Drucker, *Leipzig, Z. phys. Chem.*, **74**, 1910 (612).

[8] Sakurai, *London, J. Chem. Soc.*, **61**, 1892 (989).

[9] Landsberger, *Berlin, Ber. deut. Chem. Ges.*, **31**, 1898 (461).

[10] Walker and Lumsden, *London, J. Chem. Soc.*, **73**, 1898 (502).

[11] McCoy, H., *Baltimore, Md., Amer. Chem. J.*, **23**, 1900 (502).

[12] Smits, A., *Amsterdam, Proc. Akad. Wetens.*, **3**, 1900 (86).

[13] Rijber, *Berlin, Ber. deut. Chem. Ges.*, **34**, 901 (1060).

[14] Ludlam, *London, J. Chem. Soc.*, **81**, 1902 (1193).

[15] Erdmann and Unruh, *Hamburg, Z. anorg. Chem.*, **32**, 1902 (413).

[16] Lehner, *Berlin, Ber. deut. Chem. Ges.*, **36**, 1903 (1104).

[17] Turner, *London, J. Chem. Soc.*, **97**, 1910 (1184).

[18] Bigelow, *Baltimore, Md., Amer. Chem. J.*, **22**, 1899 (280).

[19] Cottrell, *Easton, Pa., J. Amer. Chem. Soc.*, **41**, 1919 (721).

[20] Smits, A., *Leipzig, Z. phys. Chem.*, **39**, 1902 (415); Burt, *London, J. Chem. Soc.*, **85**, 1904 (339); Drucker, *loc. cit.*; Beckmann, *Leipzig, Z. phys. Chem.*, **79**, 1912 (565); etc.

[21] Beckmann, *loc. cit.*; Washburn and Read, *Easton, Pa., J. Amer. Chem. Soc.*, **41**, 1919 (729); Sluiter, *Amsterdam, Proc. Akad. Wet.*, **17**, 1914 (1043).

[22] Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **32**, 1910 (1615).

[23] The complete apparatus, with both boiling-tube and water-filled thermometer of Pyrex glass, is furnished by Messrs. Eimer and Amend, 205 Third Avenue, New York, N. Y.

[24] Washburn and Read, *vide* note 22, *supra*.

A DIFFERENTIAL THERMOMETER

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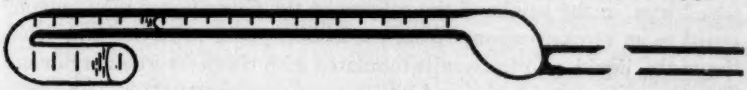
One type of differential thermometer measures the difference in temperature existing at the same location at different times; a second type measures the difference in temperature existing simultaneously at different points in space. The thermometer here described is of the latter type.



A well-known differential thermoscope of this type consists of two glass bulbs containing air, otherwise closed but communicating with each other through a U-tube partly filled with oil, whose change of level indicates change of temperature by responding to change of gas pressure within the bulbs. When this instrument is developed into a differential thermometer, certain disadvantages become apparent, of which three will here be mentioned. (1) If the manometric liquid is caused to run into one of the bulbs by accidental tilting, perhaps during transportation, then it is difficult to return the liquid into precisely the same position as it occupied when the instrument was scaled. If stopcocks are introduced in the effort to avoid this inconvenience, the cure may become worse than the disease, because of zero-creep. (2) In the presence of permanent gas, the manometric liquid becomes, in practice, not infrequently broken into threads, separated by short columns of the gas. (3) Although oils furnish very sensitive manometric liquids, their use, or, indeed, the use of any liquid other than the insensitive mercury, allows the entrance of an error that has been too little appreciated. The incidence of this error in tensimetric work has been pointed out by the writer in another connection.[1] The error in question is caused by the fact that a gas at higher pressure has a larger weight solubility than the same gas at a lower pressure. The permanent gas, always slightly soluble in manometric liquids other than mercury, therefore passes by a process of solution and diffusion from the side of higher to that of lower pressure. For this reason even stopcock-free instruments of the kind referred to suffer from slow zero-creep.

In order to avoid these and other disadvantages, all that is necessary is to abandon entirely the use of permanent gas. One selects as manometric fluid not oil but some liquid whose change of vapor pressure per degree in the range of temperature where the differential measurements are to be made is such as to cause differences of vapor pressure in the two bulbs of the thermometer that will register themselves by adequate differences of level in the manometer. The diagram, figure 1, shows one simple form

useful in ebullioscopy, made from glass tubing a few mm. in bore and having, without its handle, a length of perhaps 12 cm. Permanent gas is removed prior to sealing by the process of boiling out familiar to many who have had occasion to measure vapor pressures. For reading the difference of level of the two liquid surfaces, a mm. scale may be etched on both limbs. For many purposes, water is a suitable filling liquid; but it is obvious that the sensitiveness in any particular range of temperature may be given widely different values according to the rate of change of vapor pressure and the density of the liquid selected. The change of temperature between upper and lower bulbs that will cause a change of level of, say, 1 mm. in the height of the column of the filling liquid may be computed in an obvious manner from the known vapor pressures and densities of this liquid, and the results tabulated with temperature as argument. Thus, for water, at 57°, 80°, and 100°, these values are 0.01180°, 0.004969°, and 0.002599°, respectively.

Although the thermometers are of different general types, as indicated above, it is perhaps of interest to compare this differential thermometer with the Cavendish-Walferdin[2] metastatic type as elaborated by Beckmann,[3] and as applied in the same field, for example that of ebullioscopy. With regard to length of scale per degree, the Beckmann mercurial type is limited by the usable size of bulb, and by the permissible narrowness of the capillary, so that a centrigrade degree corresponds customarily to 40 or 50 mm. movement of the mercurial thread. The type here described is not thus limited in this respect, for a very low-boiling liquid may be used for filling. With the simple water filling, however, one degree centigrade at 80°, a temperature close to the boiling-points of the two favorite solvents benzene and ethyl alcohol, corresponds to an observed change of length of over 200 mm. In both types the length of degree varies with the actual temperature. As to range, the Beckmann type is restricted to that between −39° and +250° C.[4] While this is a much larger range than can be conveniently covered by the use of a single chosen liquid in the newer type, the simplicity of construction makes possible such a wide choice of filling liquids that a much wider range is easily available in the direction of lower as well as of higher temperatures. In comparing precision, one has to bear in mind, for the Beckmann type, possibilities of error due to (1) lack of uniformity of bore, (2) hysteresis in change of volume of bulb, (3) effect of pressure on volume of bulb, (4) sticking of mercury in capillary, (5) exposed thread, (6) difference of radiation to and from bulb, (7) departure of apparent degree from true degree. For the type here described, no one of the first six of these sources of error is important, for reasons that will be sufficiently obvious. In regard to (6), it may perhaps be said that the change with environment of radiation loss suffered by a Beckmann thermometer at temperatures far from room temperature is here largely eliminated because suffered alike by upper and

lower bulb. With regard to (7), it is indeed most necessary to employ a factor, different for each temperature, to convert observed readings to temperature; and this factor may be criticized as inconvenient to use, inaccurate in value and laborious of computation. But the use of a similar factor is likewise necessary, albeit frequently neglected, in the case of the Beckmann thermometer, whose degree, if true at 0°, is, for example, about 3% in error at 80°.[5] The accuracy of the conversion factor for the newer type is dependent in part on the accuracy with which the vapor pressure of the filling liquid is known. For such liquids as would be employed, and within the ranges of temperature that come here in question, this quantity, the vapor pressure, can now be measured to better than one part in one thousand.[6] The table that will be published for the filling liquid water, in a more comprehensive article elsewhere, was derived by differentiation from the highly satisfactory, if cumbrous, equation connecting temperature and vapor pressure of water given in the 1918 edition of the Smithsonian Meteorological Tables, and has an accuracy of just this order. The process of computing factors for, perhaps, each tenth part of a degree over a considerable range of temperature may indeed be laborious; but, once published, the factor table may be used by everyone. This inconvenience, therefore, is shifted from the shoulders of the user of the thermometer to those of him who first computed the table. It may be added that the Beckmann type is considerably more cumbrous as well as very much more fragile than the type here described, which one constructs from stout-walled Pyrex tubing.

In certain respects, therefore, it would appear that this type of differential thermometer has advantages over the Walferdin metastatic type as elaborated by Beckmann; and the question arises as to whether such other factors as are peculiar to a given application are favorable to its use. In studying its application in ebullioscopy, for example, as outlined in the article following, one finds that the important disturbing factor, peculiar to ebullioscopy in its incidence, of barometric fluctuation does not measurably affect the readings of the newer type, while such pressure fluctuations are one of the chief outstanding sources of error when the metastatic type is used. Another application in a different field may be described in the near future.

[1] Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **42**, 1920 (1951–1956).

[2] Cavendish, *London, Phil. Trans. Roy. Soc.*, **50**, 1757 (300); Walferdin, M., *Bull. Soc. geol. de France*, **13**, 1841–2 (113).

[3] Beckmann, E., *Leipzig, Zeit. physik. Chem.*, **2**, 1888 (644); **51**, 1905 (329).

[4] Cf. Staehler, A., *Leipzig, Arbeitsmethoden in der Anorg. Chemie*, **3**, i, 1913 (106).

[5] Staehler, A., *Ibid.*, p. 108.

[6] Cf. Smith, A., and Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **32**, 1910 (1412–1434).

NORMALIZED GEOMETRIC SYSTEMS

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The notion of norm or numerical value of a complex quantity, $c = a + b\sqrt{-1}$, namely, $|c| = \sqrt{a^2 + b^2}$, as it arises in algebra, has a more or less immediate generalization to more extensive matric systems. The three important properties: (1) $|c_1 + c_2| \leq |c_1| + |c_2|$; (2) $|c_1.c_2| = |c_1|.|c_2|$; (3) $c|$ is the positive square root of a positive definite quadratic form, are carried over at the expense only of replacing (2) by (2′) $|c_1.c_2| \leq |c_1|.|c_2|$ and allowing in place of (3), (3′) $|c|$ is the positive square root of a positive definite form, Hermitian or quadratic. By $c_1.c_2$ in these geometrical examples is meant the inner product[1] or a generalization of it. Two other generalizations of norm have been of great importance. The first of these is that of the theory of algebraic numbers,[2] where (1) is dropped, (2) is retained, and in place of (3) one has, Norm of c is a certain function of the nth degree, n being the order of the algebraic field. The second is that of a general theory of sets as treated for example by Fréchet,[3] where (1) is retained, (2) and (3) are dropped. The theory of integral equations as usually developed is geometrical in an infinity of dimensions and retains (1), (2′), (3′). It is noted that instances in which (1) and (2′) are retained usually keep (3′) also. Now the importance of (3′) is chiefly that it implies (1) and (2′) with the conventions as to linearity and so forth usually assumed. The converse that (1) and (2′) imply (3′) is false. It is of interest to show that most of the familiar properties of the norm may be retained, in particular (1) and (2′), when the norm is positive definite but otherwise largely arbitrary.

Three discussions bearing on this topic may be referred to. First, a geometrical study involving points but not their duals, by Minkowski, in his *Geometrie der Zahlen*.[4] The great generality of the idea of norm is there beautifully developed although it is not carried so far as it is here; but since the concept of the point dual is not brought in by Minkowski, most of the ideas here discussed are not found there. A second discussion, involving inner products, but treating only a very special case of the non-quadratic norm for an infinite number of variables is given by F. Riesz[5] in examining the convergence of bilinear forms. The third discussion involving only a scalar system, and hence without inner products, between elements of different systems is given by Kürschàk.[6] It is perhaps the most suggestive system of scalars in the literature in which $\|n\|$ may be less than n, for n a natural number.

The following treatment relates under one head the notions of convex region,[4] the triangle property,[7] the linearly homogeneous property of distance[8] or norm, conjugate norms,[5] the inner product,[1] convergence of

a bilinear form,[5] Minkowski's gauge form[4] and Schwarz's inequality[9] (so-called), as these occur in geometry, hypercomplex number theory, integral equations, and more generally, general linear analysis.[10]

The following theorem may be proved: *Every geometric system admitting a gauge set may be normalized by means of that set.* In order that there may be no ambiguity an extended sequence of definitions will be given to cover all terms used.

If P is a proposition concerning a system, S, it may be that another system, T, is such that the proposition P has a meaning for the system T. The content of the proposition may be seriously altered while its form is not affected except in the sense that S is replaced by T. We may employ the functional notations $P(S)$ and $P(T)$ to suggest that the form of the proposition is carried over unaltered from one system to the other. To avoid repetition certain propositional functions will be here listed for reference. These serve as definitions, whenever all of the terms appearing in a proposition have been themselves defined, for example, "*Reg* (L)," below, acquires a meaning only in a system in which 0_L and 1_L are defined.

The "Addition Proposition,"[11] *Add.* (R): (i) R is a system comprising elements, r, and a rule of binary combination, $+$. (ii) For any r_1, r_2, of R, $r_1 + r_2$ is a uniquely defined element of R. (iii) For any r_1, r_2, of R, $r_1 + r_2 = r_2 + r_1$. (iv) For any r_1, r_2, r_3, of R, $r_1 + (r_2 + r_3) = (r_1 + r_2) + r_3$. (v) There is an element O_R of R (also denoted by merely O), such that for every r of R, $r + O_R = r$. (vi) For a given r_1 of R, there is not more than one element r of R, such that $r_1 + r = r_1$. (vii) For a given r_1 of R, there is one and only element, r, of R such that $r_1 + r = O_R$—this element, r, is denoted by $-r_1$.

The "Multiplication Proposition," *Mult.* $(R, S, T. P)$: (i) There are systems R, S, T, P, comprising elements, respectively, r, s, t, p, and two rules of binary combination $+$ and $.$, and such that with respect to $+$, the addition proposition is valid for each of the systems. (ii) For any r of R, s of S, t of T, $r.s$ and $s.t$ are uniquely defined, and $s.t$ is an element of P. (iii) For any r_1, r_2 of R, and s_1, s_2 of S, it is true that $r_1.(s_1 + s_2) = r_1.s_1 + r_1.s_2$ and $(r_1 + r_2).s_1 = r_1.s_1 + r_2.s_1$. (iv) For any r of R, s of S, t of T, it is true that $r.(s.t) = (r.s).t$. (v) For any r of R, and s of S, it is true that $O_R.s = O_T$, and $r.O_S = O_T$.

The "Commutative Proposition," *Com.* $(C.M.L.)$: (i) C is a subsystem of M. (ii) For each c of C and l of L, $c.l = l.c$. (iii) There exists an element 1_C, of C (also denoted merely by 1) such that for every l, $1_C.l = l$.

The "Regular Proposition," *Reg.* (L): (i) The elements of L fall into two mutually exclusive subsets L_{o*} and L_∞. (ii) The elements of L_{o*} fall into two mutually exclusive subsets, L_o and L_*. (iii) O_L is an element of L_o. (iv) 1_L if it has been defined and exists, is an element of L_*. (v) For every l of L, $-l$ is in the same set as l. (vi) There exists at least one l_* other than 1_L.

The "Regular Multiplication Proposition," *R. Mult.* (R, S, T, P): (*i*) Reg. (R), Reg. (S), Reg. (T), Reg. (P). (*ii*) Mult. (R, S, T, P). (*iii*) Mult. (R_o*, S_o*, T_o*, P_o*). (*iv*) Mult. (R_o, S_o, T_o, P_o).

The "Regular Commutative Proposition," *R. Com.* (C, M, L): (*i*) Com. (C, M, L). (*ii*) For every c of C and l of L, $c_o.l_o$, $c_o.l_*$ and $c_*.l_o$ are of L_o; $c_*.l_*$ is of L_*; $c_\infty.l_*$, $c_*.l_\infty$, and $c_\infty.l_\infty$ are of L_∞. (*iii*) 1_C is of L_*. (*iv*) For every l_1 and l_2 of L, if neither l_1 nor l_2 is in L_∞, $l_1 + l_2$ is not in L_∞, and if both l_1 and l_2 are in L_o, $l_1 + l_2$ is in L_o.

The "Regular Conjugate Proposition," *R. Conj.* (C, R, S): For each r of R, there is a c of C and an s of S, such that (*i*) $r.s = s.r = c.c$; (*ii*) if r is of R_o, c is of C_o, s is of S_o; if r is of R_*, c is of C_*, s is of S_*; if r is of R_∞, c is of C_∞, s is of S_∞.

The "Normal Proposition," *Nrm.* (L): (*i*) Each l of L has associated with it a unique value, $\|l\|$. (*ii*) Reg. (L). (*iii*) For each l_o, $\|l_o\| = O$; for each l_*, $\|l_*\|$ is a positive real finite number; for each l_∞, $\|l_\infty\|$ is positively infinite. (*iv*) For each l of L, $\|-l\| = \|l\|$. (*v*) If 1_L exists, $\|1_L\| = 1$. (*vi*) There exists at least one l_* for which $\|l_*\|$ is different from unity.

The "Normal Multiplication Proposition," *N. Mult.* (R, S, T, P): (*i*) Nrm. (R), Nrm. (S), Nrm. (T), Nrm. (P). (*ii*) Mult. (R, S, T, P). (*iii*) $\|s.t\| \leq \|s\|.\|t\|$.

The "Normal Commutative Proposition," *N. Com.* (C, M, L): (*i*) Com. (C, M, L). (*ii*) For every c of C and l of L, for which $\|c\|.\|l\|$ exists, $\|c.l\| = \|c\|.\|l\|$. (*iii*) $\|1_C\| = 1$. (*iv*) For every l_1 and l_2 of L, $\|l_1 + l_2\| \leq \|l_1\| + \|l_2\|$.

The "Normal Conjugate Proposition," *N. Conj.* (C, R, S): For each r of R, there is a c of C and an s of S, such that (*i*) $r.s = s.r = c.c$, (*ii*) $\|r\| = \|c\| = \|s\|$.

The "Linear Proposition," *Lin.* (C, M, L): (*i*) Mult. (M, M, L, L). (*ii*) Mult. (M, L, M, L). (*iii*) Com. (C, M, L).

In the above, L is called a *linear system*, with M as *system of multipliers*, and C as *commutative subsystem* of M.

The "Hypernumber Proposition," *Hyp.* (C, H): (*i*) Lin. (C, C, C). (*ii*) Lin. (C, H, H).

In the above, H is called a *system of hypernumbers* with C as commutative subsystem.

The "Vector Proposition," *Vect.* (C, H, V): (*i*) Hyp. (C, H). (*ii*) Lin. (C, H, V).

In the above, V is called a *system of vectors*, with H as *associated system of hypernumbers*.

The "Regular Linear Proposition," *R. Lin.* (C, M, L): (*i*) R. Mult. (M, M, L, L). (*ii*) R. Mult. (M, L, M, L). (*iii*) R. Com. (C, M, L).

The "Regular Hypernumber Proposition," *R. Hyp.* (C, H): (*i*) R. Lin. (C, C, C). (*ii*) R. Lin. (C, H, H).

The "Regular Vector Proposition," *R. Vect.* (C, H, V): (*i*) R. Hyp. (C, H). (*ii*) R. Lin. (C, H, V).

The "Normal Linear Proposition," *N. Lin.* (C, M, L): (*i*) N. Mult. (M, M, L, L). (*ii*) N. Mult. (M, L, M, L). (*iii*) N. Com. (C, M, L).

The "Normal Hypernumber Proposition," *N. Hyp.* (C, H): (*i*) N. Lin. (C, C, C). (*ii*) N. Lin. (C, H, H).

The "Normal Vector Proposition," *N. Vect.* (C, H, V): (*i*) N. Hyp. (C, H). (*ii*) N. Lin. (C, H, V).

The "Geometric Proposition," *Geom.* (C, H, X, U): (*i*) Vect. (C, H, X). (*ii*) Vect. (C, H, U). (*iii*) Mult. (H, X, U, H). (*iv*) Mult. (H, U, X, H).

The "Regular Geometric Proposition," *R. Geom.* (C, H, X, U): (*i*) R. Vect. (C, H, X). (*ii*) R. Vect. (C, H, U). (*iii*) R. Mult. (H, X, U, H). (*iv*) R. Mult. (H, U, X, H). (*v*) R. Conj. (C, X, U). (*vi*) R. Conj. (C, U, X).

The "Normal Geometric Proposition," *N. Geom.* (C, H, X, U): (*i*) N. Vect. (C, H, X). (*ii*) N. Vect. (C, H, U). (*iii*) N. Mult. (H, X, U, H). (*iv*) N. Mult. (H, U, X, H). (*v*) N. Conj. (C, X, U). (*vi*) N. Conj. (C, U, X).

The "Gauge Proposition," *Gge.* (C, H, R, S): (*i*) For each r of R_G there is an s of S_G, such that $r.s = s.r = 1_C$, while for this s and any other element r' of R_G, $\|r'.s\| = \|s.r'\| \leq 1$. (*ii*) For each r_* of R_* there is an r of R_G, and a c of C_*, such that $r_* = c.r = r.c$.

The "Gauge Geometric Proposition," *Gge. Geom.* (C, H, X, U): (*i*) R. Geom. (C, H, X, U). (*ii*) N. Hyp. (C, H). (*iii*) There exists a subset X_G of X_*, and a subset U_G of U_*. (*iv*) Gge. (C, H, X, U). (*v*) Gge. (C, H, U, X).

The "Division Proposition," *Div.* (C, S, T): For each s of S_*, there is at least one t of T_*, such that (*i*) $s.t = t.s. = 1_C$, (*ii*) $\|s\|.\|t\| = 1$.

The "Norm Product Proposition," *N. Prod.* (R): For every r_1, r_2 of R, for which $\|r_1\|.\|r_2\|$ is defined, $\|r_1.r_2\| = \|r_1\|.\|r_2\|$.

A system (C, H, X, U) is said to be a *geometric system* if Geom. (C, H, X, U) is valid with respect to it. It is further said to *admit a gauge set*, if Gge. Geom. (C, H, X, U) also is valid. To *normalize* a geometric system is to define $\|x\|$ and $\|u\|$ in such a manner that N. Geom. (C, H, X, U) is valid, while any geometric system for which N. Geom. (C, H, X, U) holds is said to be a *normal geometric system*.

A geometric system admitting a gauge set may be normalized but leads to a special type of normal geometric system, since for any geometric system admitting a guage set, the following additional propositions may be proved: Div. (C, C, C), Div. (C, H, H), N. Prod. (C), N. Prod. (H), and for the normalized system obtained the following also are provable: Div. (C, X, U), Div. (C, U, X). For the general normal geometric system none of these six propositions may be true.

To normalize a geometric system admitting a guage set, define for every x_G and u_G, $\|x_G\| = 1$, $\|u_G\| = 1$, and for every $c.x_G$ and $c.u_G$, $\|c.x_G\| = \|c\|$, $\|c.u_G\| = \|c\|$. The theorem then follows without difficulty.

For the general normal geometric system, the *relative inclination*, θ, of two elements, x of X_*, and u of U_*, may be defined by, $\|x.u\| = \|x\|.\|u\| \cos\theta$. Thus x of X_*, and u of U_* are mutually orthogonal if and only if $\|x.u\| = O$. Two elements, x of X_* and u of U_*, are mutually *conjugate* if and only if $x.u = u.x = c.c$ while also $\|x\| = \|u\| = \|c\|$. Two elements, x of X_*, and u of U_*, are mutually *reciprocal* if and only if $x.u = u.x = 1_C$ while also $\|x\|.\|u\| = 1$. The sets (x) and (u) for which $\|x\| = 1$, and $\|u\| = 1$, respectively, are Convex. The relation $\|r_1 + r_2\| \leq \|r_1\| + \|r_2\|$ is called the Triangle Inequality of the norm. The relation $\|c.l\| = \|c\|.\|l\|$ is called the Linearly Homogeneous Property of the norm. The expressions $\|x\|$ and $\|u\|$ are said to be Conjugate Norms and when continuous, each is a "Gauge Form." The expressions $x.u$ and $u.x$ are Inner Products. Each of the bilinear forms $x.u$ and $u.x$ "converges" if $\|x\|$ and $\|u\|$ are finite, since $\|x.u\| \leq \|x\|.\|u\|$, and $\|u.x\| \leq \|u\|.\|x\|$, which are statements of the general form of Schwarz's Inequality.

The following possibilities for a normal geometrical system may be emphasized: (*i*) The product among hypernumbers need not be commutative. (*ii*) The product involving two x's or two u's need not have a meaning. (*iii*) The system C may be an integral system in which division is not in general possible. (*iv*) $\|n_C\|$ may be less than n, where by n_C is meant $1_C + 1^C + \ldots + 1_C$ to n terms, for $n > 1$. (*v*) The conjugate of a given element need not be unique. (*vi*) The set of elements (x) for which $\|x\| = 1$, may be dense but not continuous, as for example the rational points on a circle. In particular, the above theory is applicable to the Geometry of Numbers of Minkowski,[4] to a system where C is a Kürschak valuated field,[6] and to a system where H is a quaternion field.[12]

While in every normal geometric system each x of X_* has a conjugate, u of U_*, which has again the given x as its conjugate, the conjugate relation is not in general a simple one. The geometric systems for which (3′) is satisfied are identified by the semi-linear property that if x_1 and u_1 be conjugates, and x_2, u_2 be conjugates, then $c_1.x_1 + c_2x_2$ and $c'_1.u_1 + c'_2.u_2$ will be conjugates where c_1, c_2, c'_1, c'_2 are of C, while c and c' are themselves conjugates in a more elementary sense.

[1] Due to Grassmann, *Geometrische Analyse*, 1847, paragraph 7, p. 16; cf. Gibbs, *Vector Analysis* (E. B. Wilson).

[2] Suggested by Gauss, Dirichlet, *Werke*, I, p. 539. Extended use by Kronecker, "De unitatibus complexis," *Werke* I, p. 14.

[3] Fréchet, M., Sur quelques points..., *Rend. Circ. M. Palermo*, **22**, 1906 (1–74).

Consult A. D. Pitcher and E. W. Chittenden, "On the Foundations of the Calcul Fonctionelle of Fréchet," *Trans. Amer. Math. Soc.*, **19**, 1918 (66–78).

[4] Minkowski, H., *Geometrie der Zahlen*, p. 9 (Ed. 1910), Leipzig.

[5] Riesz, F., *Les systèmes d'equations linéaires*, Paris (1913).

[6] Kürschàk, J., Ueber Limesbildung..., *Crelle*, **142**, 1913 (211).

[7] Proved in elementary geometry for triangles, namely (1) above.

[8] Identified since C. Wessel (1799), Gauss, and Hamilton.

[9] Moore, E. H., *Fifth Int. Cong. Math.* **1912**, I (253).

[10] Moore, E. H., *Bull. Amer. Math. Soc.*, (Ser. 2), **18**, 1912 (334–362), and later papers.

[11] Cf. Moebius, Der barycentrische Calcul, (1897), *Werke*, I.

[12] Cf. Hurwitz, A., *Zahlentheorie der Quaternionen*, Berlin (1919).

PROBLEMS OF POTENTIAL THEORY

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1. *The Equations of Laplace and Poisson.*—As is well known, Bôcher considered the integral form of Laplace's equation:[1]

$$\int \frac{\partial u}{\partial n}\, ds = 0, \tag{1}$$

and showed that it was entirely equivalent to the differential form

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0 \tag{2}$$

for functions u continuous with their *first* partial derivatives over any "Weierstrassian" region (as Borel would call it[2]); in fact he showed that any such solution of (1) possessed continuous derivatives of all orders and satisfied (2) at every point. One can go still further, and consider solutions of (1) which have merely summable derivatives, and of the first order, with practically the same result.

THEOREM I.—If the function u is what we shall call a "potential function for its gradient vector ∇u,"[3] the components of the latter being summable superficially in the Lebesgue sense, and if the equation

$$\int \nabla_n u\, ds = 0 \tag{1}$$

is satisfied for every curve of a certain class,[4] then the function u has merely unnecessary discontinuities, and when these are removed by changing the value of u in the points at most of a point set of superficial measure zero, the resulting function has continuous derivatives of all orders and satisfies (2) at every point.

Let us pass on to the equation

$$\int \frac{\partial u}{\partial n}\, ds = \int \rho\, d\sigma \tag{3}$$

in which a curvilinear integral on the left is equal to a superficial integral on the right, and this equality is a generalization of Poisson's equation

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = \rho(x,y). \tag{4}$$

But we need not limit ourselves in the right hand member to quantities which are the integrals of functions ρ; instead we may take the right hand member to be any sort of additive function of point sets $f(e)$[5] (not necessarily absolutely continuous as in (3) or even continuous), or any sort of additive function of curves in the plane $f(s)$,[6] of limited variation. More precisely, we consider the equation

$$\int \nabla_n u \, ds = F(s) \tag{3'}$$

in which $F(s)$ is an additive function of curves in the plane, of limited variation, with discontinuities "of the first kind."

The difference of any two solutions of (3') is a solution of (1'), and, therefore, part of the study of (3') is the study of a particular solution. Such a particular solution is found to be the function

$$u(M_1) = \frac{1}{2\pi}\int_\Sigma \log \frac{1}{r}\, df(e) \tag{5}$$

defined in terms of a Lebesgue-Stieltjes integral. In this equation M_1 is the point of coördinates x_1, y_1, M the point of coördinates x, y which is the argument of the integration, and r the distance between them; in measuring angles the sense of r is taken as M_1M. This function may be shown to be the potential function of a gradient vector of which the component in the direction α is given by

$$\nabla_\alpha u(M_1) = \frac{1}{2\pi}\int_\Sigma \frac{\cos \alpha r}{r}\, df(e). \tag{6}$$

The vector given by (6) may be shown to be a solution of (3') for every curve of the class Γ (specified below).

In two dimensions, a Stieltjes integral may be defined equally well in terms of both sorts of functional, and a function of curves used as well as a function of point sets for the function of limited variation. And thus if Σ' is a region enclosed in Σ, with boundary S' (a curve of class Γ), we may speak of the function

$$u'(M_1) = \frac{1}{2\pi}\int_{\Sigma'} \log \frac{1}{r}\, dF(s), \tag{5'}$$

which is identical with the function given by (5) for all points interior to Σ', provided that the equality

$$F(s) = f(e) \quad (e = \text{set of points inside } s), \tag{5''}$$

holds for any s of Γ on which $F(s)$ is continuous as a function of curves.

Methods of making correspondences of type (5'') will be discussed below.

2. *Various Forms of Green's Theorem.*—Let $F(s)$ and $G(s)$ be two functions of curves with discontinuities of the first kind, and $U(M)$ and $V(M)$ two solutions of the equations

$$\int \nabla_n U ds = F(s)$$

$$\int \nabla_n V ds = G(s),$$

which may be written in the form given by (5) or (5′) plus harmonic functions (i. e., solutions of (1′) after the unnecessary discontinuities have been removed). With respect to $F(s)$ and $G(s)$ let us introduce the symbols $T_F(s)$ and $T_G(s)$ to stand for their total variation functions. Then we have the following rather general result.

THEOREM II.—If the discontinuities of $F(s)$ and $G(s)$ are of the first kind, a sufficient condition that the equation

$$\int_\sigma (\nabla_x U \nabla_x V + \nabla_y U \nabla_y V) d\sigma = \int_\sigma U dG(s) - \int_s U \nabla_n V ds$$

$$= \int_\sigma V dF(s) - \int_s V \nabla_n U ds \qquad (7)$$

shall hold for all regions σ and all boundaries s of Γ, internal to Σ', is the existence of the quantity

$$\int_{\Sigma'} \log \frac{1}{r'_{M_1 M}} dT_F(s) dT_G(s).$$

A vector φ which satisfies the equation corresponding to (3′)

$$\int_s \varphi_n ds = F(s) \qquad (8)$$

for every curve of Γ may be called a *polarization vector* for the distribution $F(s)$; it is not necessary that such vectors shall, as in the examples already given, have potential functions. Those that we have already given satisfy also certain restrictions of integrability which we denote by condition N, as follows:

Condition N. Any component of φ is summable superficially, and the normal component is summable along any curve of Γ; in particular, the integral of the absolute value of φ_n, along any curve of Γ or finite number of mutually exclusive curves remains finite, less than some fixed number N, provided that the total length of the curves remains finite, less than some fixed number s_0.

We have then the following theorems:

THEOREM III.—Let $G(s)$ be an arbitrary function of curves, additive and of limited variation,[7] and let $\psi(M)$ be a polarization vector for it which satisfies condition N; further let $u(M)$ be a function continuous over Σ' with its first partial derivatives. Then for every s of class Γ the following equation is valid:

$$\int_\sigma u dG(s) = \int_s u \psi_n ds + \int_\sigma \left(\frac{\partial u}{\partial x} \psi_x + \frac{\partial u}{\partial y} \psi_y \right) d\sigma \qquad (9)$$

THEOREM IV.—If $\psi(M)$ satisfies condition N and $u(M)$ is continuous and a potential function for its vector gradient in Σ, the equation

$$\int_\sigma u dG(s) = \int_s u\psi_n ds + \int_\sigma (\nabla_x u\psi_x + \nabla_y u\psi_y) d\sigma \qquad (9')$$

remains valid provided that one of the following hypotheses (α), (β) or (γ) be imposed:

(α) $\nabla u(M)$ is bounded.

(β) $\psi(M)$ is bounded.

(γ) The quantities $\{\nabla u(M)\}^2$ and $\{\psi(M)\}^2$ are summable superficially.

If in this theorem we put $u(M) = \log 1/r$, we obtain:

THEOREM V.—If $\psi(M)$ satisfies condition N the equation

$$\int_\sigma \log\frac{1}{r} dG(s) = \int_s \log\frac{1}{r}\psi_n ds + \int_\sigma \left\{\psi_x \frac{\partial}{\partial x}\log\frac{1}{r} + \psi_y \frac{\partial}{\partial y}\log\frac{1}{r}\right\} d\sigma \qquad (10)$$

is valid, given the region σ, for all points M_1 except possibly those which form a point set of superficial measure zero.

One or two more special theorems are perhaps interesting. If in Theorem II we put $V = \log 1/r$, we obtain the equation

$$2\pi U(M_1) = \int_s \left\{U\frac{\partial}{\partial n}\log\frac{1}{r} - \log\frac{1}{r}\nabla_n u\right\} ds + \int_\sigma \log\frac{1}{r} dF(s) \qquad (11)$$

which holds whenever $U(M_1)$ is the derivative of its own superficial integral, and, therefore, except for the points of a set of superficial measure zero.

If in Theorem IV we put

$$\psi = \lambda\varphi$$

where λ is a scalar point function, so that the vector φ satisfies the equation

$$\int_s \lambda\varphi_n ds = G(s)$$

then equation (9′) reduces to the following:

$$\int_\sigma \lambda\{\nabla_x u\varphi_x + \nabla_y u\varphi_y\} d\sigma = -\int_s \lambda u\varphi_n d\sigma + \int_\sigma u dG(s). \qquad (12)$$

These theorems provide for the Stieltjes integral with respect to a function of curves a representation in terms of a Lebesgue integral and a curvilinear integral. The curvilinear integral is essentially a curvilinear integral, depending only on the contour, and differs thus from the integral around general boundaries defined by P. J. Daniell,[9] which is a "frontier integral" not uniquely determined by the contour itself, but by some superficial point set.

The theorems of this section remain true if for σ is substituted a set of points measurable superficially in the sense of Borel, for s its frontier, and for $F(s)$, $G(s)$ the corresponding additive functions of point sets $f(e)$, $g(e)$, the frontier integrals being defined according to the method of Daniell. We shall come later to another possible method of determining frontier integrals.

3. *Definitions and Examples.*—It is desirable to render more precise some of the notions which we have used.

A curve of class Γ is a simple closed rectifiable curve composed of a finite number of pieces, each piece having a definite direction at every point; for each curve there is a constant Γ such that the following inequality holds.

$$\int_s \frac{|\cos nr|}{r_{M_1M}}\, ds < \Gamma,$$

wherever the point M_1 may be. For a curve which is everywhere convex, for instance, Γ may be taken as 2π.

With respect to gradient vector and potential function we have the following definition. If $A(M)$ is a vector point function whose components in two fixed directions (and therefore in any fixed direction) are summable, and $u(M)$ is a scalar point function whose integrals may be defined along any curve of class Γ, then A is spoken of as a *gradient* of u, and u as a *potential function* of A provided the equation

$$\int_\sigma A_\alpha d\sigma = \int_s u d\alpha' \tag{13}$$

is satisfied for every s of Γ and for every α, the subscript α being used to represent a fixed direction and α' that direction advanced by $\pi/2$.

It is sufficient that (13) should hold for two distinct directions α in order to hold for every direction.

The curvilinear integral in (13) is an example of what may be called an *absolutely continuous* function of curves. For the purpose of this article we say that an additive function of curves is of *limited variation* if it is the difference of two additive functions of curves, each one positive or zero for every curve of class Γ.

Every curve s of Γ determines a set e of points interior to the region σ which it bounds. We shall consider correspondences between functions of curves $F(s)$ and functions of points sets $f(e)$ such that for every curve on which $F(s)$ is continuous the equation

$$f(e) = F(s) \tag{14}$$

holds. Given $F(s)$ it may be shown that $f(e)$ is uniquely determined over all sets measurable in the sense of Borel, simply by means of (14).

On the other hand the equation (14) is not sufficient to determine $F(s)$, given $f(e)$. The discontinuities of $F(s)$ may still be distributed in various ways. The $F(s)$ which is defined by the formula

$$F(s_1) = \frac{1}{2\pi} \int_{s_1} ds_1 \int_\Sigma \frac{\cos nr}{r}\, df(e) \tag{15}$$

has all of its discontinuities of the *first kind;* that is, if a portion, s', which has everywhere a tangent, forms part both of s_1 and s_2, otherwise mutually exterior, a possible discontinuity upon s' would be shared equally by

$F(s_1)$ and $F(s_2)$; and if a point P is a vertex for s_1, a portion of the possible discontinuity at P proportional to the angle at the vertex is taken up by $F(s_1)$.

In order to illustrate this correspondence, take the following example. Let Σ be the square $0<x<1$, $0<y<1$; and to the points M^i of rational coördinates in this Σ assign positive numbers $p(M^i)$ in such a way that when the points are arranged in countable order, the series of numbers will be convergent; and make the definition

$$f(e) = p(e) = \Sigma_i p(M^i), \tag{16}$$

where the sum is extended over all the M^i in the set e. Introduce now an auxiliary function $\mu(\theta,M)$, which for a given point M depends on an angle θ made with a fixed direction, and which is such that the quantity $\int_0^{2\pi} \mu(\theta,M)d\theta$ is everywhere unity. Consider the quantity

$$H(M,\theta_1,\theta_2) = \int_{\theta_1}^{\theta_2} \mu(\theta,M)d\theta.$$

For the purpose of defining $F(s)$ every point of s may be considered temporarily as a vertex, the tangents forward and backward from M making, respectively, angles θ_1,θ_2 with the fixed direction. Then the equation

$$F(s) = \Sigma'_\sigma p(M^i) + \Sigma_s H(M^i,\theta_1,\theta_2)p(M^i),$$

where the first summation takes all the points M^i interior to σ and the second takes all the points M^i on the boundary s, satisfies the equation of correspondence (14) and defines an additive function of curves of limited variation which is discontinuous on every curve which contains a rational point. In general, the discontinuities of $F(s)$ will not be of the first kind; in order to make them so, and thus satisfy the equation (15), it is sufficient to put $\mu(\theta,M) = 1/2\pi$.

The directional derivative of a point function $u(M)$ is not necessarily a vector, merely on the basis of its existence. If, however, this derivative for two directions, say $\partial u/\partial x$ and $\partial u/\partial y$, is summable superficially and satisfies for these two directions and all curves of Γ the equation (13), then the vector which has these two quantities for its components in the two directions will be a gradient vector, and the original function its potential function. Yet it is simpler for the purpose of proving theorems and less artificial, to use directly a generalized partial derivative which has itself vectorial properties.

We say that $D_\alpha u$, *the generalized derivative in the direction* α of $u(M)$, is the limit, if such limit exists, of the expression

$$D_\alpha u = \lim_{\sigma=0} \frac{1}{\sigma} \int_s u d\alpha' \tag{17}$$

where the fixed direction α' makes an angle of $\pi/2$ with the fixed direction α, and σ denotes the area enclosed by s; it is understood that σ tends

toward 0 only in such a way that the ratio σ/d^2, where d is the diameter of σ, remains different from zero by some positive quantity.

It is a theorem that the expression (6) is the generalized derivative of the expression (5) except at the points of a set E_0 of superficial measure zero, which may be chosen independently of the direction α. The function defined by (5) is therefore a solution of the equation

$$\int_s D_n u \, ds = F(s) \tag{18}$$

for any curve which does not contain points of E_0 of more than linear measure zero. The transition from this equation to the equation

$$\int_s \frac{\partial u}{\partial n} \, ds = F(s)$$

involving derivatives in the customary sense, is possible for classes of curves defined in terms of curvilinear coördinates, by means of the identity between a double and an iterated integral in these coördinates.

4. *A Double Integration by Parts.*—The Green's theorem from the point of view of section 2 may be regarded as an integration by parts of the multiple Stieltjes integral with respect to one dimension only. It is perhaps worth while to state the theorem which one obtains by a complete integration by parts of the double integral.

Let $u(M)$ be a continuous point function of limited variation[10] and let $q(M) = G(\bar{s})$ where $\bar{s}$ is the rectangle whose diagonally opposite vertices are M and the origin. Then if s is any simple closed regular curve, and points P_i with coördinates x_i, y_i are taken round the curve such that $|x_{i+1}-x_i|<\delta, |y_{i+1}-y_i|<\delta$ the following integrals have meaning:

$$\int u d_y q = \lim_{\delta=0} \Sigma_i u(x_i,\eta_i)\{q(x_i,y_{i+1})-q(x_i,y_i)\} \qquad y_i \leqq \eta_i \leqq y_{i+1},$$

$$\int u d_x q = \lim_{\delta=0} \Sigma_i u(\xi_i,y_i)\{q(x_{i+1},y_i)-q(x_i,y_i)\} \qquad x_i \leqq \xi_i \leqq x_{i+1}, \tag{19}$$

and the identity

$$\int_\sigma udq = \int_\sigma qdu + \int_\sigma dqu - \int_s ud_y q + \int_s ud_x q \tag{19'}$$

is valid.[11] In this equation the quantity $\int dqu$ stands for the total variation of qu over the region σ.

5. *Applications.*—Consider the function

$$W(z_1) = \frac{-1}{2\pi i} \int_\Sigma \frac{df(e)}{z-z_1} \tag{20}$$

where z denotes the quantity $x + iy$, where $f(e) = f_1(e) + if_2(e)$ is a complex additive function of point sets, and the integral has the meaning:

$$W(z_1) = U(M_1) + iV(M_1)$$

with

$$U(M_1) = \frac{1}{2\pi}\int \frac{y-y_1}{r^2}\,df_1(e) - \frac{x-x_1}{r^2}\,df_2(e)$$

$$V(M_1) = \frac{1}{2\pi}\int \frac{x-x_1}{r^2}\,df_1(e) + \frac{y-y_1}{r^2}\,df_2(e).$$

From this evaluation follows the equation

$$\int_{s_1} W(z_1)dz_1 = F(s_1), \tag{21}$$

where $F(s)$ is the function of curves with discontinuities of the first kind which is equivalent to $f(e)$.

If we extend the notion of generalized derivatives to functions of a complex variable, it turns out that what corresponds to the quantity

$$\frac{\partial W}{\partial x} + i\frac{\partial W}{\partial y}$$

is the limit:

$$\lim_{\sigma=0}\frac{1}{i\sigma}\int W(z)dz,$$

which is merely the superficial derivative, where it exists, of the additive function of point sets $f(e)/i$. But this quantity exists in Σ except possibly at the points of a set of superficial measure zero. At a point where this superficial derivative itself vanishes it seems opportune to follow the direction of Borel's concept, and speak of the function $W(z)$ as *monogenic*.

If $\kappa(z)$ is a function of a complex variable, analytic in Σ, and $Q(z)$ is a solution of the equation

$$\int_s Q(z)dz = F(s)$$

and equal to $W(z)$ plus an analytic function, the equation

$$\int_s \kappa Q dz = \int_\sigma \kappa dF(s)$$

is satisfied. In particular, by taking as $\kappa(z)$ the function $1/(z-z_1)$, it may be deduced that except possibly at the points of a set of superficial measure zero the following identity holds:

$$Q(Z_1) = \frac{1}{2\pi i}\int_s \frac{Q(z)}{z-z_1}\,dz + \frac{1}{2\pi i}\int_\sigma \frac{dF(s)}{z-z_1} \tag{22}$$

The function given by (20) is the unique derivative of a certain functional of open curves in the plane, considered as a function of the endpoint of the curve. We have, in fact, $W(z) = dZ(1|z)/dz$, where

$$Z(1|z_1) = \frac{1}{2\pi i}\int_\Sigma \log(z-z_1)df(e). \tag{23}$$

Here the values of arctan $y-y_1/x-x_1$ are taken, say, as the principal values for a particular value of $z_1 = z_0$, thus defining log $(z-z_0)$ for z in Σ; log $(z-z_1)$ is then defined in general by means of the curve 1 which connects z_0 with z_1.

A different sort of application of these ideas is to the Dirichlet problem: to determine a harmonic function throughout a Weierstrassian region by assigned frontier values. For this purpose consider an arbitrary simply connected T region as defined by Osgood[12] whose boundary consists of more than one point; for simplicity we may as well restrict it to the finite domain.

Let M_o be an interior point of T and $g(M_o,M)$ its Green's function. Let $h(M_o,M)$ be the conjugate function of $g(M_o,M)$. These functions are both harmonic at every point of T, the point M_o excepted; and the following facts can be stated with reference to the frontier of T:

To an accessible point on the frontier corresponds a value of h, $h = C$ (and perhaps more than one value), but to two different accessible frontier points cannot correspond the same value C.[13] We see then that if a value of h corresponds to an accessible frontier point, the point is uniquely determined. But it can be shown that all values of h except possibly some which constitute a set of measure zero actually do correspond to accessible points on the frontier.

For a given point M_o of T we thus set up a correspondence between the curves $h\ (M_o,M) = C$ and the accessible points on the frontier of T.

Consider functions $u(M)$ which are limited and continuous in T, and whose first partial derivatives with their squares are summable over T. Form the integral

$$-\int_{P_1}^{P_2} u(M)\frac{\partial g}{\partial n}\,ds = \int_{h_1}^{h_2} u(M)dh(M_o,M) \qquad (24)$$

along a curve joining a point, P_1, on $h = C_1$ to a point, P_2, on $h = C_2$ and composed of points M given by the relation $g(M_o,M) = \psi(h)$, where $\psi(h)$ is an arbitrary continuous function of values of h between C_1 and C_2. As $\psi(h)$ is let approach zero remaining always not-negative and less than some finite N, it is seen by comparison with additive functions of point sets that the integral (24) has a limiting value; and the Stieltjes integral in the right hand member defines in the limit an absolutely continuous function $U(h)$ of h_2, which is therefore the integral of its derivative with respect to h, this derivative being a summable function $\bar{u}(h)$. It may be shown that as M travels along a curve, $h = C$, we have lim $u(M) = \bar{u}(C)$ except for values of C which constitute a set of linear measure zero. In other words, the frontier values of $u(M)$, taken in this sense, are summable with respect to h, and the frontier integral is properly a Stieltjes integral of frontier values.

Vice versa, given $\bar{u}$ limited and summable with respect to h on the frontier of T there is one and only one bounded function $u(M)$, continuous and harmonic in T, with first partial derivatives and their squares summable over T, and such that it takes on the frontier values $\bar{u}(h)$ "almost everywhere" in the above-described manner.

No single point M_0 need be preferred. If $\bar{u}(M)$ is summable with respect to $h(M_0,M)$ on the frontier of T when M_0 is some definite point in T, it is summable on the frontier of T with respect to $h(M_1,M)$, M_1 being any point of T.[14]

[1] *Proc. Amer. Acad. Sci., Boston*, **41**, 1905–06.

[2] Borel, E., *Leçons sur les fonctions monogènes*, Paris, 1917, p. 10.

[3] Evans, *Rend. R. Accad. Lincei*, (Ser. 5), **28**, 1919 (262–265).

[4] For example it is sufficient to consider merely rectangles. See also the class Γ below.

[5] de la Vallée Poussin, C., *Integrales de Lebesgue*, Paris, 1916, p. 57.

[6] Volterra, V., *Leçons sur les fonctions de lignes*, Paris, 1913, chapt. II. It is to be noted that the definitions of continuity in the case of functions of curves and in the case of functions of point sets do not correspond at all to the same situation.

[7] The discontinuities need not be of the first kind.

[8] By $\{\psi(M)\}^2$ is meant the quantity $\{\psi_x(M)\}^2 + \{\psi_y(M)\}^2$.

[9] *Bull. Amer. Meth. Soc.*, **25**, November, 1918 (65–68).

[10] de la Vallée Poussin, C., *loc. cit.*, p. 98; *Trans. Amer. Math. Soc.*, **16**, 1915 (493).

[11] This identity is given for the special case of a rectangle, where the integrals (19) do not have to be used, by W. H. Young, *Proc. London Math. Soc.*, (Ser. 2), **16**, 1917.

[12] Osgood, *Lehrbuch der Funktionentheorie*, Leipzig, 1912, p. 151.

[13] Osgood and Taylor, *Transactions of the American Mathematical Society*, **14**, 1913 (277–298).

[14] A complete exposition of the theorems of this paper will appear in an early issue of the *Rice Institute Pamphlet*.

THERMO-ELECTRIC ACTION AND THERMAL CONDUCTION IN METALS: A SUMMARY

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I shall now undertake to show in brief what I have accomplished in the series of papers which for some years I have been publishing in these PROCEEDINGS in relation to thermo-electric action and thermal conduction in metals.

Starting with the hypothesis of dual electric conduction, that is, conduction maintained in part by the passage of electrons from atomic union to atomic union during the contacts of atoms with positive ions, and in part by "free" electrons in the comparatively weak fields of force called the inter-atomic spaces, I derived[1] an equation giving the conditions of steady state in a detached bar hot at one end and cold at the other, and two equations for the conditions of equilibrium at a junction of two metals.

For the detached bar the steady state is a current of associated electrons up the temperature gradient and an equal current of free electrons down the temperature gradient. This involves a freeing of electrons from atomic unions, ionization, at the hot end of the bar, with absorption of heat, and re-association at the cold end, with evolution of heat. Evidently this is a process of conveying heat, and the question at once arises

whether it is capable of accounting for the whole or any considerable part of thermal conduction in metals.

At the junction of two metals, on the other hand, the conditions of equilibrium permit no cyclic or circulatory motion of the electrons.

In a later paper[2] I introduced the following assumptions: That n, the number of free electrons per cu. cm. of the metal, is expressed by the equation

$$n = zT^q, \tag{1}$$

where T is absolute temperature while z and q are constants. That $(k_f \div k)$, the ratio of free-electron conductivity to total conductivity, is given by the equation

$$(k_f \div k) = C + C_1 t + C_2 t^2, \tag{2}$$

where t is temperature on the ordinary centigrade scale and C, C_1, C_2, are constants.

That the heat of ionization, in ergs, per electron is

$$\lambda' = \lambda_c' + 2.5RT, \tag{3}$$

where λ_c' is a constant[3] and R is the gas-constant for a single molecule.

In a still later paper[4] I rejected (3) and put in its place

$$\lambda' = \lambda_c' + sRT, \tag{3'}$$

where s is a constant never less than 2.5. This change involved the revision of all the tables of numerical values contained in the paper in which equation (3) was used.

Equations (1), (2) and (3') introduced for each metal seven characteristic constants, z, q, C, C_1, C_2, λ_c' and s, but z may for the most part be left out of consideration, as the definite numerical value of n is needed only incidentally[5] in what follows.

To determine the six other constants for any metal we need six equations. Let us suppose that we know for each metal the value of the Thomson effect, σ, the value of the heat conductivity at 0° C., θ_0, and at 100° C., θ_{100}.

My expression for σ is in the form

$$\sigma = K + (K_1 + K_2 t)T, \tag{4}$$

in which K, K_1 and K_2 are determined functions of q, C, C_1, etc. Bridgman's experiments give me the values of K, K_1 and K_2, for many metals, and so from the Thomson effect I get three equations, which are too long to be given here.

My expression for thermal conductivity is

$$\theta = \frac{R^2}{e^2}\left(\frac{\lambda_c'}{R} + sT\right)\frac{k_a k_f}{k}(s + q - 1.5), \tag{5}$$

in which k_a, the "associated-electron" conductivity, is $(k - k_f)$. With the known values of θ_0 and θ_{100} I get two more equations involving the six characteristic quantities to be determined for each metal.

Thus for two metals, α and β, with twelve characteristic quantities to be determined, I have ten equations given by the properties of the metals, each metal being considered separately. When the two metals are brought into contact at 0° C. and again at 100° C., I have two Peltier-effect equations of the form

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \lambda_\beta - \left(\frac{k_f}{k}\right)_\alpha \lambda_\alpha \qquad (6)$$

one for each temperature, where λ_β is the heat, in ergs, required to free $(1 \div e)$ electrons within β, and λ_α has a like meaning for α.

Thus I have twelve equations to determine the twelve constants in question.

If my theory were perfect and my experimental data complete, every constant could be found exactly, or to any desired degree of precision, by means of the equations here mentioned; but neither of these conditions is fulfilled. It is unlikely, for example, that equation (1) holds strictly through any considerable range of temperature. The experimental data I have used are doubtless incorrect to some extent, and in several places I have had to fill observational gaps by rather hazardous methods, particularly in values of thermal conductivity. Somewhat arbitrarily I have chosen to treat Bridgman's values of σ as strictly correct, though he does not so regard them. I have done the same with regard to the available values of k_0, k_{100}, θ_0, and Π_0. Accordingly the values of θ_{100} and Π_{100} worked out from my equations are subject to the accumulated errors of theory and data, and it is not very disconcerting to find them differing considerably in some cases from the observed values or those indicated by other evidence.

If the question is raised why values of the constants cannot be found that will satisfy all of the equations, even if some of the data are inaccurate, the answer is that not all values are available for these constants, thus C, q, λ_c', and s must all be positive quantities.

Below are given for each of many metals, and for two alloys, the values of the six constants that I have hit on to account, as well as may be, for the observed or estimated values of the Thomson effect, thermal conductivity, and Peltier effect with respect to bismuth, in these substances. It is to be remembered that the algebraic sign which I give to the Thomson effect in any metal is opposite to the one ordinarily used; for example, I call σ positive in iron and negative in copper. The Peltier effect, Π, is given as the amount of heat, in ergs, absorbed by $(1 \div e)$ electrons in going from the metal in question to bismuth. Thermal conductivities are given in calories/cm., sec., deg. C. The constant part, λ_c', of λ' is given in ergs; δ_c is the "ionizing potential," in volts, corresponding to λ_c'; δ_0 and δ_{100}, respectively, are the ionizing potentials, in volts, for the total work of ionization at 0° C. and at 100° C.; k is electric conductivity in absolute measure. The numbers in the horizontal lines marked *Calc.*

are those which my formulae yield when the given values of the constants are put into them.

ALUMINIUM

C	$C_1 \times 10^8$	$C_2 \times 10^8$	q	s	$\lambda'_c \times 10^{18}$	δ_c	δ_0	δ_{100}
0.0846	−2.85	6.19	1.45	5.64	176	0.011	0.142	0.190
	σ (in ergs/° C.)		θ_0	θ'_{00}	$\Pi_0 \times 10^{-4}$	$\Pi_{100} \times 10^{-4}$	$k \times 10^8$	$k_{100} \times 10^8$
Data	$(-0.016 + 0.006t)T$		0.477	0.492	202	263	380	265
Calc.	$(-0.016 + 0.006t)T$		0.478	0.445	201	210		

BISMUTH

C	$C_1 \times 10^8$	$C_2 \times 10^8$	q	s	$\lambda'_c \times 10^{18}$	δ_c	δ_0	δ_{100}
0.19°	−80.4	0	1.2	4.35	1088	0.068	0.169	0.206
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0 \times 10^{-4}$	$\Pi_{100} \times 10^{-4}$	$k_0 \times 10^8$	$k_{100} \times 10^8$
Data	$-3.2T$		0.0202	0.0161	0	0	9.30	6.46
Calc.	$-3.2T$		0.0201	0.0164	0	0		

COBALT

C	$C_1 \times 10^8$	C_2	q	s	$\lambda' c \times 10^{18}$	δ_c	δ_0	δ_{100}
0.134	175	0	1.55	5.26	32	0.002	0.125	0.170
	σ (ergs/° C.)		θ_0 (?)	θ_{100} (?)	$\Pi_0 \times 10^{-4}$	$\Pi_{100} \times 10^{-4}$	$k_0 \times 10^8$	$k_{100} \times 10^8$
Data	$7.8T$		0.161(?)	0.164(?)	156	172	102	74.7
Calc.	$7.8T$		0.160	0.177	154	117		

COPPER

C	$C_1 \times 10^8$	C_2	q	s	$\lambda'_c \times 10^{18}$	δ_c	δ_0	δ_{100}
0.068	−16.6	0	1.49	6.8	64	0.004	0.162	0.221
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0 \times 10^{-4}$	$\Pi_{100} \times 10^{-4}$	$k_0 \times 10^8$	$k_{100} \times 10^8$
Data	$-0.966T$		0.920	0.908	211	280	650	455
Calc.	$0.966T$		0.928	0.866	211	229		

GOLD

C	$C_1 \times 10^8$	$C_2 \times 10^9$	q	s	$\lambda'_c \times 10^{18}$	δ_c	δ_0	δ_{100}
0.070	−16.3	8.7	1.49	6.7	48	0.003	0.159	0.217
	σ (ergs/° C)		θ_0	θ_{100}	$\Pi_0 \times 10^{-4}$	$\Pi_{100} \times 10^{-4}$	$k_0 \times 10^8$	$k_{100} \times 10^8$
Data	$(-0.934 + 0.00t)T$		0.699	0.703	211	280	490	351
Calc.	$(-0.934 + 0.00t)T$		0.696	0.666	210	227		

IRON

C	$C_1\times10^6$	$C_2\times10^3$	q	s	$\lambda' c\times10^{15}$	δ_{∞}	δ_0	δ_{100}
0.02	12.1	19.9	1.2	15	128	0.008	0.348	0.487
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-6}$	$\Pi_{100}\times10^{-6}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$(1.78+0.0516t)T$		0.163	0.151	247	310	78	48.1
Calc.	$(1.78+0.0516t)T$		0.164	0.146	251	226		

MAGNESIUM

C	$C_1\times10^6$	$C_2\times10^6$	q	s	$\lambda' c\times10^{15}$	δ_C	δ_0	δ_{100}
0.061	−13.8	0	1.499	6.8	608	0.038	0.196	0.255
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-6}$	$\Pi_{100}\times10^{-6}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$-0.008T$		0.376(?) (?)	?	203	266	240	?
Calc.	$-0.008T$		0.374		202	220		

MOLYBDENUM

C	$C_1\times10^6$	$C_2\times10^3$	q	s	$\lambda' c\times10^{15}$	δ_C	δ_0	δ_{100}
0.053	−64.4	10.8	1.3	8	176	0.011	0.197	0.266
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-6}$	$\Pi_{100}\times10^{-6}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$(-4.33+0.015t)T$		0.43(?)	0.42(?)	219	319	274	191
Calc.	$(-4.33+0.015t)T$		0.43	0.358	217	252		

NICKEL

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_C	δ_0	δ_{100}
0.132	84.9	0	1.6	5.0	176	0.011	0.127	0.170
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-6}$	$\Pi_{100}\times10^{-6}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$0.0356T$		0.143	0.138	155	187	93	62.5
Calc.	$0.0356T$		0.142	0.134	153	136		

PALLADIUM

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_C	δ_0	δ_{100}
0.083	64.3	0	1.6	6.51	139	0.0087	0.160	0.216
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-6}$	$\Pi_{100}\times10^{-6}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$3.52T$		0.165	0.182	188	232	100	75.9
Calc.	$3.52T$		0.165	0.179	188	182		

PLATINUM

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_c	δ_0	δ_{100}
0.0808	50.8	0	1.6	6.24	176	0.011	0.157	0.210
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$2.67T$		0.164	0.173	195	245	110	79.3
Calc.	$2.67T$		0.167	0.170	194	195		

SILVER

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_c	δ_0	δ_{100}
0.0663	−14.2	0	1.49	7.1	64	0.004	0.169	0.230
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$-0.864T$		1.009	0.992	210	279	670	476
Calc.	$-0.864T$		1.018	0.964	209	226		

THALLIUM

C	$C_1\times10^6$	$C_2\times10^8$	q	s	$\lambda' c\times10^{15}$	δ_c	δ_0	δ_{100}
0.0625	3.48	2.69	1.48	7.3	160	0.01	0.180	0.243
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$(0.268+0.0034t)T$		0.090[8]	0.096[8]	208	271	57	43.9
Calc.	$(0.268+0.0034t)T$		0.090	0.094	209	221		

TIN

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_c	δ_0	δ_{100}
0.0654	2.36	0	1.51	6.66	368	0.023	0.179	0.236
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$0.134T$		0.157	0.145	204	266	105	72.6
Calc.	$0.134T$		0.154	0.142	204	220		

TUNGSTEN

C	$C_1\times10^6$	C_2	q	s	$\lambda' c\times10^{15}$	δ_c	δ_0	δ_{100}
0.042	−35	0	1.48	11.4	40	0.0025	0.268	0.366
	σ (ergs/° C.)		θ_0(?)	θ_{100}(?)	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$-341T$		?	?	207	285	140	106
Calc.	$-341T$		0.352	0.335	208	234		

ZINC

C	$C_1\times10^6$	C_2	q	s	$\lambda'_c\times10^{16}$	δ_c	δ_0	δ_{100}
0.0613	16.7	0	1.55	7	240	0.015	0.178	0.238
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_0\times10^{-}$	$k_0\times10^4$	$k_{100}\times10^{16}$
Data	$0.99T$		0.266	0.262	211	274	180	127
Calc.	$0.99T$		0.266	0.258	212	225		

CONSTANTAN

C	$C_1\times10^6$	C_2	q	s	$\lambda'_0\times10^{16}$	δ_c	δ_0	δ_{100}
0.135	141	0	1.55	6.65	48	0.003	0.158	0.215
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^{-4}$	$\Pi_{100}\times10^{-4}$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$7.94T$		0.052	0.064	108	106	20.4	20.4
Calc.	$7.94T$		0 052	0.076	108	55		

MANGANIN

C	$C_1\times10^6$	$C_2\times10^8$	q	s	$\lambda'_0\times10^{16}$	δ_c	δ_0	δ_{100}
0.050	−98	4.07	1.51	9.65	54	0.0034	0.228	0.311
	σ (ergs/° C.)		θ_0	θ_{100}	$\Pi_0\times10^4$	$\Pi_{100}\times10^4$	$k_0\times10^6$	$k_{100}\times10^6$
Data	$(-0.828-0.0067t)T$		0.051	0.063	207	275	23.8	23.8
Calc.	$(-0.828-0.0067t)T$		0.051	0.068	206	223		

The preceding tabulation deals with every metal and alloy for which I have the necessary data, except cadmium, and for this metal, as I have shown elsewhere,[10] there is some reason for doubting the correctness of the data, Bridgman's value for σ in cadmium being about ten times as large as that found by other investigators.

In the table that follows, γ is the estimated ratio, expressed in per cents, of the number of free electrons to the number of atoms, including the positive ions, within the metal at 0° C. In arriving at the given value of γ I have made use of the equation

$$k = \frac{nlce^2}{4RT} \qquad (7)$$

for the free-electron conductivity. The second member differs from Drude's familiar expression for the total conductivity, supposed by him due entirely to the free electrons, only in having 4 instead of 6 in the denominator. I have taken l, somewhat arbitrarily but not without regard to what others have done in this particular, as equal to ten times the centre to centre distance of adjacent atoms.

In columns II and III are given, in absolute units, the values of the potential gradient urging the associated electrons up the temperature gradient, at 0° C. and 100° C., respectively. P is potential due to electric charge, and (dP/dT) seems open to electrostatic measurement. P_a is potential due to differential attraction of the unequally heated metal for the associated electrons, and (dP_a/dT) does not seem within reach of direct experiment at present. Integrated from 0° C. to 100° C., $d(P + P_a)/dT$ gives differences of potential ranging from about 0.0026 volt in iron to about 0.0065 volt in bismuth and in cobalt and about 0.008 volt in constantan.

Column IV gives values of the "ionizing potential," in volts, within the metals at 0° C., and column V shows what these values would be at 2727° C., or 3000° absolute, if the equation

$$\lambda' = \gamma'_c + sRT$$

held all the way to that temperature.

Nothing exact can be expected from such an extrapolation, which takes no account of melting or of vaporization, but it is interesting to note that the values of δ thus obtained are of the same order of magnitude as those found by direct experiment on the vapors of metals, though still somewhat smaller than these latter values.

Column VI shows, in calories, the amount of heat absorbed by the free ions and by the process of ionization in heating 1 cu. cm. of the metal 1° C. in the neighborhood of 0° C. The former of these quantities is $1.5R\gamma n$, and the latter $dn/dT.\lambda' = q n\lambda'/T$, each reduced to calories. Column VII gives the thermal capacity, per cu. cm., of the metals as found by experiment.

	I γ %	II $\left[\frac{d(P+P_a)}{dT}\right]_0$	III $\left[\frac{d(P+P_a)}{dT}\right]_{100}$	IV δ at 0° C.	V δ at 2727° C.	VI	VII
Aluminium	10.5	−4070	−4050	0.142	1.46	0.212	0.54
Bismuth	1.0	−6620	−6340	0.169	1.18	0.009	0.29
Cobalt	4.9	−6120	−6920	0.125	1.35	0.139	0.86
Copper	11.7	−3970	−3870	0.162	1.75	0.388	0.80
Gold	11.4	−4030	−3940	0.159	1.72	0.260	0.60
Iron	0.7	−2530	−2680	0.348	3.85	0.038	0.85
Magnesium	11.1	−3550	−3550	0.196	1.78	0.224	0.40
Molybdenum	4.4	−3540	−3110	0.197	2.06	0.099	0.70
Nickel	3.1	−5790	−6160	0.127	1.29	0.093	0.89
Palladium	2.6	−4720	−5080	0.160	1.68	0.069	0.57
Platinum	2.9	−4410	−4680	0.157	1.69	0.078	0.67
Silver	15.2	−4050	−3960	0.169	1.82	0.365	0.58
Thallium	1.8	−3910	−3960	0.180	1.88	0.027	0.36
Tin	3.2	−3700	−3720	0.179	1.73	0.052	0.39
Tungsten	1.9	−4120	−3770	0.268	2.92	0.072	0.64
Zinc	3.2	−3720	−3820	0.178	1.81	0.093	0.64
Constantan	0.7	−7780	−8590	0.158	1.71	0.024	0.85
Manganin	0.3	−4180	−4060	0.228	2.47	0.013	0.77

Evidently any number given in column VI should be smaller than the corresponding number given in column VII; and this is the case; but, for aluminium, copper, gold, and magnesium the ratio approaches one-half, and for silver it is greater than one-half. This is a larger value of the ratio than seems probable; that is, one might expect for these metals, if the values of column VI are true, greater departures from the law of Dulong and Petit than they really show. It is to be remembered, however, that the values of γ, upon which the numbers given in column VI depend, are based on the assumption that the mean free path of the free electrons within a metal is in all cases ten times the centre to centre distance of adjacent atoms. If we assume longer paths, we get correspondingly smaller values in columns I and VI. According to Compton and Ross[11] a photo-electrically excited electron can move in gold about twenty times the centre to centre distance of the atoms.

In view of the fact that the known specific heats of metals are in some cases smaller and in some cases larger than the law of Dulong and Petit requires, one may allow himself considerable latitude in dealing with the distribution of heat energy among the various degrees of freedom of the atoms. It is perhaps worth while to note that the numbers given in column VI would be larger if calculated for a temperature above 0° C., as this fact suggests at least an explanation of the general increase in the specific heats of metals with rise of temperature. More exact knowledge than we now have concerning the rate of this increase is greatly to be desired.

Doubtless my theory of heat conduction will be criticized as failing to deal in any general way with the Wiedemann-Franz law. This law is by no means exact. According to Jäger and Diesselhorst the ratio $(\theta \div k)$ varies, at 18°C., from 6.36×10^{10} in aluminium to 9.64×10^{10} in bismuth, while the temperature coefficient of this ratio varies from 0.15% in bismuth to 0.46% in platinum and palladium. In dealing theoretically with the relations of thermal to electrical conductivity we may proceed in either of two ways. We may seek for such a mechanism of conduction and such a general formula as will give the W.-F. law and then undertake to show why the individual metals depart from it, or we may proceed at first without any regard to this law but finally treat each metal in such a way as to explain its more or less approximate conformity with the law. The latter is the method I have followed.

I do not claim complete success in this undertaking. Some of the expedients I have adopted—for example, the values of s which I have assumed—are open to doubt. It may be that the mechanism which I have imagined and described, convection of heat by means of a circulatory electric current, can account for only a part, perhaps a small part, of the

total heat conduction of metals; but I trust that enough has been done to show that the possibilities of this mechanism are worthy of serious consideration.

I propose next to consider how far the ideas set forth in this paper will go toward explaining the various "transverse" electro-magnetic and hermomagnetic effects in metals.

[1] These PROCEEDINGS for April, 1918, pp. 98–103. I there used in turn "hypothesis A" and "hypothesis B" concerning the behavior of the free electrons as a gas. In nearly all that follows I have used "hypothesis A" which is that, aside from electric influences, the free electrons tend to equality of gas pressure throughout the bar, whereas "hypothesis B" assumes that they tend to follow the law of "thermal effusion."

[2] These PROCEEDINGS for March, 1920, pp. 139–154.

[3] Strictly, λ'_0 was used here instead of λ'_c, with the same meaning.

[4] These PROCEEDINGS, **6**, 1920 (617).

[5] It seems probable that in dealing with the conditions at the junction of two metals we really need to use the conception of number-density of free electrons in the "co-volume" of each metal. In fact, n may without harm be interpreted as having this meaning in all my formulas except the one, taken from Drude, in which I express the free-electron conductivity in terms of mean free path, mean velocity, etc., of the free electrons. See the latter part of this paper, where γ, the grade of ionization, is estimated.

[6] Estimated by use of the Wiedermann-Franz ratio (average for 12 metals) applied to k_0 and k_{100}.

[7] Mean value, according to Lorenz (1881) between 0° C. and 100° C.

[8] See note under Cobalt.

[9] θ_{18} is given as 0.35 on the authority of Coolidge.

[10] These PROCEEDINGS, **6**, 1920 (617).

[11] *Physical Review*, May, 1919.